Suppressing transmembrane-pressure rise by pulse dosing of submicron super-fine powdered activated carbon: effects of filtration flux, coagulant types, and coagulant-dose timing during precoating

Short title: Suppressing TMP rise by SSPAC pulse-dosing

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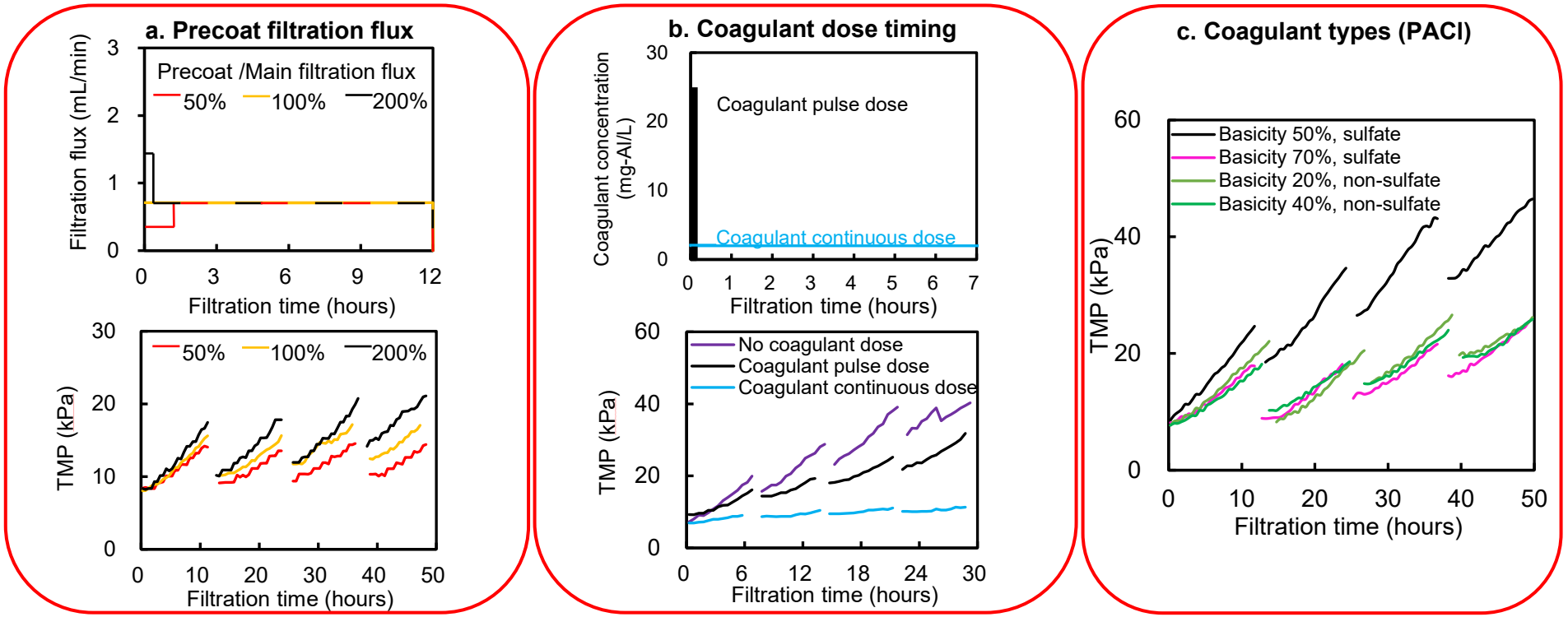
Research highlights

- Pulse-dosed coagulant inadequately suppressed transmembrane pressure (TMP) rise
- Pulse dosing of submicron-sized powdered activated carbon (SSPAC) was effective
- TMP rise was not suppressed by short-term precoating and filtration with high flux
- Dosing coagulants throughout filtration is recommended to suppress TMP rise
- Basicity of coagulant PACl affects TMP rise when SSPAC is pulse-dosed


a. Precoat filtration flux
Filtration flux (mL/min)
Precoat /Main filtration flux
50%
100%
200%
Filtration time (hours)
TMP (kPa)
50%
100%
200%
Filtration time (hours)
b. Coagulant dose timing
Coagulant concentration (mg-Al/L)
Coagulant pulse dose
Coagulant continuous dose
Filtration time (hours)
TMP (kPa)
No coagulant dose
Coagulant pulse dose
Coagulant continuous dose
Filtration time (hours)
c. Coagulant types (PACl)
TMP (kPa)
Basicity 50%, sulfate
Basicity 70%, sulfate
Basicity 20%, non-sulfate
Basicity 40%, non-sulfate
Filtration time (hours)

ABSTRACT

Submicron-sized powdered activated carbon (SSPAC, diameter 200 nm) dosed in a pulse after coagulation pretreatment has recently been found to effectively mitigate membrane fouling and thus to suppress the rise of transmembrane pressure (TMP) in the microfiltration process because SSPAC has a higher capacity to adsorb membrane foulants, such as natural organic matter, than conventional PAC and a precoat layer formed by SSPAC on the membrane surface retards membrane fouling. This study investigated the effects of the filtration flux during precoating, the timing of coagulant dosing, and the types of coagulants on the suppression of TMP rise by pulse-dosed SSPAC. The TMP rise was insensitive to the filtration flux during precoating. However, the efficacy of the SSPAC was sensitive to the use of the coagulant polyaluminum-chloride (PACl). Unlike pulse dosing of SSPAC, pulse dosing of coagulant led to excessive aggregation and settling of SSPAC and insufficient formation of a precoating layer. The best filterability was achieved when the coagulant was dosed continuously in the entire operation period. It is also effective to use treated water for feeding during the preparation stage. For sulfated PACl, high basicity (70%), with its high charge neutralization capacity, was preferred to medium basicity (50%). Meanwhile, the TMP rise was more effectively suppressed by non-sulfated PACl with a low-to-medium basicity (20–40%) than zero or high basicity (70%). This behavior was explained by the fact that, as the basicity increases, hydrolysis of the coagulants is lessened, but the charge neutralization effect becomes stronger.

Keywords: microfiltration, membrane fouling, precoat, polyaluminum chloride, basicity, water treatment

1. Introduction

During the membrane filtration process in drinking water treatment, natural organic matter (NOM) accumulates on/inside the membrane surface, clogs/constricts the membrane pores, and gradually fouls the membrane. The accumulation of NOM decreases filterability (increases transmembrane pressure [TMP] in the case of a constant filtration flux) and makes the filtration process consume more energy [1–3]. It has recently been reported that a hydrophilic fraction of the NOM with molecular weights of more than 10,000 Da (also known as biopolymer) is the major contributor to membrane fouling [4–7]. It is therefore necessary to protect the membrane from foulants, in particular biopolymers, during the filtration process to prevent a decrease of filterability and to reduce the energy consumed during the filtration operation. A pretreatment method that involves powdered activated carbon (PAC, median diameter 10–30 μm) adsorption combined with coagulation treatment has proven to be effective in removing NOM and mitigating membrane fouling and has been widely applied in the practice of full-scale treatment plants [8–11]. Although combining PAC adsorption with coagulation certainly has a positive effect, more studies are required to increase the efficiency of membrane fouling mitigation and reduce the energy consumed during filtration.

Coating membrane surfaces to mitigate membrane fouling has been widely studied in some areas of water treatment [12–15], but there have been few studies of coating with inexpensive materials applicable to drinking water treatment [16,17]. It has recently been reported that grinding normal PAC into a submicron size (median diameter 200 nm) can greatly increase its capacity to adsorb NOM (especially biopolymer), and when submicron-sized PAC (SSPAC) is dosed in a pulse at the beginning of each filtration in a submerged membrane system, a precoating layer of SSPAC forms on the membrane surface as the filtration proceeds. This precoating layer protects the membrane by enhancing its adsorption capacity and straining ability versus ordinary PAC and thereby mitigating the membrane fouling [18,19]. Furthermore, the introduction of a coagulant eliminates the concern that SSPAC itself may foul the membrane [18]. In fact, the precoating layer can be easily peeled off by periodic hydraulic backwashing [18]. However, this mitigation of membrane fouling by pulse dosing of SSPAC with a coagulant has been studied under only one condition: pulse dosing of SSPAC at the

beginning, continuous dosing of one type of polyaluminum-chloride (PACl) coagulant with a high basicity (70%) during the filtration period, and one constant filtration flux. The effects of the timing of coagulant addition and the filtration flux for precoating have not been explored. Moreover, it is reasonable to infer that the type of coagulant would also influence the degree of mitigation of membrane fouling when coagulation pretreatment is combined with pulse dosing of SSPAC because coagulation pretreatment is considered to be effective in mitigating membrane fouling, and the pretreatment efficiency is highly dependent on the type of coagulant [20–22].

The goal of this study was to investigate ways to add SSPAC and coagulant in order to mitigate membrane fouling and suppress TMP rise during filtration in a submerged membrane system. We conducted experiments that involved filtering river water with periodic backwashing, and we investigated how the flux during the precoating period, dose timing of PACl, and the basicity of the PACl influenced the rise of TMP.

2. Materials and methods

2.1. Water samples

Water from the Wanigawa River (Wanigawa Water Purification Plant, Ibaraki, Japan) was sampled in May and November of 2019 (Designated as Water-1 and Water-2, respectively) and 2020 (Water-3 and Water-4, respectively). The water was transported to the laboratory and stored at a temperature of 4 °C. Raw water for experiments was prepared by returning the temperature to 20 °C and passing the water through a coarse filter with a pore size of 10 μm (coated cellulose acetate membrane filter, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) to remove large particles.

Concentrations of dissolved organic carbon (DOC), biopolymer, humic substances, and ultraviolet absorbance at 260 nm (UV260) were used to characterize the water quality of the filtrates and raw water (after being pre-filtered through a 0.45-μm PTFE membrane). The DOC concentration was measured with a TOC analyzer (Model 900, Sievers Instruments, Boulder, CO, USA). The UV260 was measured using a UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). A high-performance liquid

chromatography (HPLC) system (1100 series, Agilent Tech, Tokyo, Japan) consisting of a single column (Toyopearl HW-50S, 250 mm × 20 mm, Tosoh Inc., Tokyo, Japan), an injection system (flux of 1.2 mL/min), a UV detector, and a TOC analyzer (M9e, Central Kagaku Corp., Tokyo, Japan) was configured to measure the concentrations of biopolymer and humic substances in the DOC [5]. Table 1S of the Supplementary Information (SI) shows the water quality metrics.

2.2. Activated carbon

Activated carbon was prepared by the same procedure used in a previous study to ensure consistency of experimental conditions [18]. A wood-based PAC (Taiko-W, Futamura Chemical Co., Ltd., Nagoya, Japan) with a median diameter (D50) of 12 μm was mixed with pure water (Milli-Q water, Merck KGaA, Darmstadt, Germany) to make a PAC slurry with a PAC concentration of 15% (w/w). The slurry was milled in a closed chamber filled with alumina balls for 6 h to reduce the D50 to less than 4 μm. The resultant slurry was ground with a bead mill filled with 0.2-mm-diameter beads for 2 h (LMZ015, Ashizawa Finetech, Ltd., Chiba, Japan) to obtain SSPAC with a D50 of 200 nm.

The SSPACs were mixed with a dispersant (Triton X-100, Kanto Chemical Co., Inc., Tokyo, Japan) and sonicated, then their particle sizes were measured with a laser-light-scattering instrument (Microtrac MT3300EXII, Nikkiso Co., Inc., Tokyo, Japan) [23]. Figure 1S of the SI shows the size distributions of the SSPACs.

2.3. Coagulants

Sulfated polyaluminum chloride (PACl) coagulants with a basicity of 50% and sulfate ion content of 3% w/w (PACl-B50S) or basicity of 70% and sulfate ion content of 2% w/w (PACl-B70S) were obtained from a coagulant manufacturer (Taki Chemical Co., Hyogo, Japan). Non-sulfated coagulants with basicities of 0%, 20%, 40%, 50%, and 70% (designated as PACl-B00, -B20, -B40, -B50, and -B70, respectively) were produced in the authors' laboratory by using basically the same method used to produce the PACl-B70S and B50S ($Al(OH)_3$ dissolution method) [24]. The $AlCl_3$ H_2O solution was mixed

with $Al(OH)_3$ powder (Guaranteed Reagent, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) and heated in a microwave labstation (ETHOS TC, Milestone S.r.l., Sorisole (BG), Italy) at 150 °C for 3 h. The solution was then centrifuged at 3000 rpm (1140 *g*) for 10 min, and the supernatant was filtered through a 0.45-µm PTFE membrane filter (Toyo Roshi Kaisha, Ltd., Tokyo, Japan). The filtrate was transferred to a bottle that was placed on a hot plate/magnetic stirrer at a rotation rate of 600 rpm and heated to a temperature of 75 °C. An amount of sodium carbonate (Guaranteed Reagent, FUJIFILM Wako Pure Chemical Corporation) calculated to produce the targeted basicity was dripped into the solution. The basicity was calculated with Eq. (1):

$$\text{Basicity (\%)} = \frac{[OH^-]}{3[Al]} \times 100 \quad (1)$$

where [Al] is the aluminum concentration measured with an inductively coupled plasma mass spectrometer (ICPMS, 7700x, Agilent Technologies, Inc., Santa Clara, Ca, USA), and OH^- is the concentration of hydroxyl groups calculated from the mass balance of $Al(OH)_3$ and titrated sodium carbonate. Table 2S of the SI shows the conditions maintained during production of the coagulant.

2.4. Submerged membrane filtration with coagulant and SSPAC dosing

2.4.1 Experiment setup

Figure 1 shows the experiment setup, which was unchanged from a previous study [18]. Raw water was fed by a peristaltic pump at the flow rate of 0.64 mL/min into a static mixer, and coagulants were fed through another line at a flow rate of 0.07 mL/min. The coagulant dosage was 2 mg-Al/L. After a dose of coagulant, NaOH was injected into the line to bring the pH to 7.5, and the water flowed into a submerged tank where a hollow fiber PVDF (polyvinylidene fluoride) membrane with a 0.1-µm pore size (Asahi Kasei Corp., Tokyo, Japan) was suspended. The membrane was sealed at one end so that suction pressure at the other end resulted in filtration. The suction pressure was recorded by a digital pressure meter (GC61, Nagano Keiki Products, Tokyo, Japan), and the water temperature was measured with a digital thermometer (LR5011, Hioki E.E. Corp.,

187 Nagano, Japan). Filtration was conducted at a constant flux of 1.7 m/day (70.8 L m^{-2} h^{-1})
188 except for the initial period of filtration. Backwashing was conducted with pure water
189 every 7 or 12 hours with a peristaltic pump at 50 kPa. After backwashing followed by
190 drainage, the next round of filtration was begun. SSPAC was dosed in a pulse at the
191 beginning of each filtration at a dosage of 5 mg/L. Dosage was equated to the mass of
192 SSPAC divided by the volume of treated water. The experiments were conducted at a
193 controlled temperature of 20 °C, and the filtrates were sampled with a fraction collector
194 for water quality analysis.
195
196 *2.4.2 Filtration with changing precoat filtration flux*
197 The filtration flux at the beginning of the filtration period (= precoat filtration flux in
198 this study) and the filtration flux during the remainder of the filtration (main filtration
199 flux) were considered separately. The duration of the precoat filtration (precoating period)
200 was equated to the hydraulic retention time of the submerged tank, so that the precoating
201 period was inversely proportional to the precoat filtration flux (Fig. 2S, SI). The precoat
202 filtration flux was set to 50%, 100%, 200%, 300%, 400%, 500%, or 633% of the main
203 filtration flux (1.7 m/day) (Fig. 3S, SI). These runs were designated as PF-50%, etc.,
204 where the percentage indicates the precoat filtration flux as a percentage of the main
205 filtration flux. In some experiments, a portion of the water in the submerged tank was
206 sampled right after the SSPAC dose and before initiation of precoating. Another portion
207 was sampled at the end of precoating. The turbidities of the water samples were measured
208 after a one-min sonication. Precoating efficiency was defined as the SSPAC on the precoat
209 divided by the total amount of dosed SSPAC and was estimated as 1.0 minus the ratio of
210 turbidity after/before precoating. It was assumed that SSPAC was mainly responsible for
211 the turbidity.
212
213 *2.4.3 Filtration with changing coagulant dose timing*
214 The timing of the coagulant dose was changed in some experiments as follows (Figure
215 2):
216 Dose-1: coagulant was dosed in a pulse immediately after pulse dosing of SSPAC
217 but was not dosed after that during the filtration.
218 Dose-2: coagulant was continuously dosed during the preparation period (water was

fed into the submerged tank for the start of filtration) and for 1 h after the start of filtration but was not after that during the filtration.

Dose-3: coagulant was continuously dosed for only 1 h after the start of filtration (it was not dosed at other times).

Dose-4: coagulant was dosed during the whole period (preparation and filtration periods).

Dose-5: coagulant was dosed only during the filtration period (not fed during the preparation period).

The dosage of coagulant was controlled so that the dose divided by the volume of treated water was constant and equal to 2 mg-Al/L.

3. Results and discussion

3.1. Effects of precoat filtration flux on TMP rise

Figure 3 shows changes of TMP in the filtration experiments with a changing precoat filtration flux wherein the filtration flux was decreased/increased after pulse dosing of SSPAC and then restored to the original filtration flux. In the A series run (Panel A of Fig. 3: the dosages of SSPAC and coagulant were 5 mg/L and 2 mg-Al/L, respectively), the PF-50% resulted in the smallest TMP rise. PF-100% resulted in the second-lowest TMP rise for the first 24 hours, but the PF-400% and 100% resulted in the second-lowest TMP rise at 48-h. For comparison, panel A of Fig. 4S of the SI shows the TMP rise due to hydraulically irreversible fouling, i.e., the difference of the TMPs at the beginning of two consecutive batches of filtration with backwashing in between. The TMP rise due to hydraulically irreversible membrane fouling was the lowest in the experiment with the lowest initial filtration flux (PF-50%), followed by PF-100% and PF-400%. The TMP rises due to hydraulically irreversible membrane fouling were high in the four runs with precoat filtration fluxes that exceeded 100% (PF-200%, 300%, 500%, and 633%), except for PF-400%. In the B series of runs (Panel B of Fig. 3 and Panel B of Fig. 4S: the dosages of SSPAC and coagulant were 1 mg/L and 1 mg-Al/L, respectively), the TMP rose more

rapidly than in the A series because the lower dosages of SSPAC and coagulant more likely caused membrane fouling. Neither PF-50% nor 100% was found to be superior in suppressing TMP rise when compared with PF-200% and 300%. The data from all runs are shown in Fig. 5S of the SI.

The slower and constant precoat filtration fluxes (PF-50% and 100%) seemed to be effective when the addition of SSPAC and coagulant was sufficient to basically mitigate membrane fouling. Then, additional experimental runs were conducted to compare PF-50% and 100%. In these experiments, the amounts of filtered water were adjusted so that they were the same by slightly (by 5.2%) prolonging the filtration time of the PF-50% run. The same filtration time would have resulted in slightly different filtration volumes between the low and high precoat filtration fluxes and might have caused different degrees of membrane fouling. Panel A of Fig. 6S of the SI shows that PF-50% suppressed TMP rise slightly more than PF-100%, but the difference was small. There was almost no significant difference in the TMP rise due to hydraulically irreversible fouling between PF-50% and 100% (Panel B of Fig. 6S of the SI).

Overall, the experimental results were not completely consistent, but they suggested that a high precoat filtration flux did not help to suppress a TMP rise. High precoat filtration fluxes have been thought to result in faster formation of a precoating layer that would protect the membrane from fouling, but the actual TMP rise was similar to or higher than the TMP rise with a lower precoat filtration flux. Unlike continuous dosing, pulse dosing of SSPAC created an overdose at the beginning of filtration so that more of the NOM that caused membrane fouling was adsorbed by the SSPAC (Fig. 7S, SI). With pulse dosing of SSPAC, therefore, the water in the submerged tank before the start of filtration seems to have a low concentration of biopolymers, etc. In this sense, it may be possible to further prevent membrane fouling due to NOM if filtrate (treated water) instead of the raw water is returned to the submerged tank during the preparation period before filtration begins. Filtration experiments were therefore conducted in which raw water or filtrate was treated similarly by coagulation and SSPAC and then fed to the submerged tank for starting membrane filtration membrane (Dose-4 in Section 2.4.3). After filtration started, the raw water was fed to the submerged tank in both experiments, but to equalize net membrane-filtered water production the filtration time was prolonged by 5.2% when filtrate had been returned than when raw water had been normally fed. The

results are shown in Figure 4 (Fig. 8S of the SI). Two runs were conducted, but in both runs, the TMP rise of irreversible fouling was lower when the submerged tank was initially fed with filtrate than raw water, indicating that less NOM concentration during precoating period helps prevent membrane fouling. However, this approach (returning filtered water to the feed side) is not efficient in water production, and its application should be considered in practice with this in mind.

On the other hand, the mechanism that explains why a higher precoat filtration flux did not mitigate membrane fouling efficiently could be related to the portion of the precoat layer that was tightly attached to the membrane rather than to NOM fouling. Formation of a precoat layer that can be removed by backwashing is considered to be a key factor that suppresses TMP rise [18]. Another explanation might be related to the absence of a relationship between precoating efficiency and precoat filtration flux inferred from the fact that the precoating efficiencies of SSPAC in PF-100% and 300% were almost the same (~60%), as shown in Fig. 9S of the SI. In addition, the fact that the entire amount of pulse-dosed SSPAC was not applied for precoating might be related to the affinity of the SSPAC for the membrane. A slow precoat filtration flux may be effective in suppressing a TMP rise, but it was not effective, for example, when the SSPAC and coagulant dosages were low. Reducing the precoat filtration flux causes the precoat layer to not be very tightly bound to the membrane and thereby facilitates removal during backwashing. However, the longer time required for completion of precoating by SSPAC deposition increases the time during which the membrane is exposed to foulant. This problem is more likely to be troublesome when the SSPAC and coagulant dosages are low.

3.2. Effects of coagulant dose timing on TMP rise

Figure 5 shows the rise of the TMP with time in experiments at different coagulant doses. Experiments at each dose were conducted 2–4 times, and Fig. 5 shows the average values (Fig. 10S in the SI shows all the data). The TMP rise without SSPAC and coagulant dosing reached 40 kPa after 28 hours (Control in Fig. 10S, SI). The TMP rose to 22 kPa after the same filtration time with pulse dosing of coagulant after pulse dosing of SSPAC (Dose-1 in Fig. 2). Continuous dosing of coagulant for only one hour from the start of filtration

(Dose-3) resulted in a 10-kPa TMP rise. The rise of the TMP was only around 5 kPa in the three cases of (i) continuous, short-term dosing of coagulant when water was fed to the submerged tank and for one hour after the start of filtration (Dose-2), (ii) continuous dosing of coagulant while water was fed to the submerged tank and during the whole filtration period (Dose-4), and (iii) continuous dosing of coagulant during only the filtration period (Dose-5). Continuous dosing of coagulant while water was fed to the submerged tank throughout the whole filtration period (Dose-4) was the most effective way to constrain the TMP rise among all the dosing methods. The fact that the increase in TMP at Dose-2, 3, 4, and 5 was much lower than at Dose-1 (0.8 kPa/h), and the difference between Dose-2 (0.2 kPa/h), 3 (0.37 kPa/h), 4 (0.16 kPa/h), and 5 (0.24 kPa/h) was small, means that the addition of coagulant in the early stages of filtration (the initial 1 hour) was important in preventing the increase in TMP. Furthermore, the low TMP increase at Dose-2 and 4 suggests that it is also effective to add coagulant before the start of filtration. From these results, it was interpreted that the initial coagulation treatment contributes to the precoat layer formed in the early stages of filtration, which is easily detached by hydraulic backwash.

Figure 6 shows the concentrations of biopolymers and humic substances in the filtrates. Biopolymers and humic substances were mostly removed by filtration with or without SSPAC and coagulant dosing, meaning that these were retained in the submerged membrane tank. They probably accumulated on/inside and fouled the membrane leading to rapid TMP rise when SSPAC and coagulant were not dosed. Where they are held in the membrane-submerged tank is important for membrane fouling, but their removal rate and the degree of membrane fouling are not directly related. Dose-4 achieved better removal of biopolymers than any other method. In the case of humic substances, however, there were no significant differences among the dose methods. The success of Dose-2 (continuous, short-term dosing of coagulant) indicated that dosing of coagulant in the early stages of filtration (but not pulse dosing) was effective, and coagulant dosing could be omitted in the latter stages of filtration.

PACl is effective in removing hydrophobic matter composed of large molecules [25,26], and SSPAC has been reported to have a large capacity to adsorb onto DOC, especially biopolymers [18]. The combination of SSPAC along with coagulation is therefore expected to be effective in suppressing a rise of TMP due to multiple effects. After SSPAC is dosed in a pulse at the beginning of each filtration process, a precoating layer is formed on the membrane surface, and the precoating strains out a portion of foulants [18]. However, when the coagulant was dosed in a pulse as SSPAC, we observed

deposition of many black floc particles at the bottom of the tank, as shown in the photograph of the submerged tank taken during filtration (Fig. 11S, SI). High concentrations of coagulant led to excessive coagulation of SSPAC, the settling of SSPAC to the bottom of the tank, and finally to the suppression of SSPAC from forming a precoat. The investigation of coagulant dose timing indicated that continuous dosing of coagulant during the feeding of water into the submerged tank and throughout the whole filtration period did the best job of suppressing a TMP rise. Another point to note here (Fig. 5) is that (i) the continuous dosing of coagulant during the feeding of water into the submerged tank and for one hour after the start of filtration and (ii) the continuous dosing of coagulant during only the filtration period were similarly effective in suppressing a rise of TMP. This result indicated that providing sufficient coagulant during the formation of the SSPAC precoating layer could help to eliminate the side effect of hydraulically irreversible fouling caused by the strong bonding between the SSPAC precoating layer and the membrane. Coagulation dosing during the period of water feeding (Dose-2 and Dose-4 in Fig. 2) was therefore necessary to ensure formation of a loose, porous precoating layer.

3.3. Effects of coagulant (PACl) types on TMP rise

Sulfated PACl (B50S and B70S) and non-sulfated PACl with a variety of basicities (B00, B20, B40, B50, and B70) were used in the experiments with pulse dosing of SSPAC and continuous PACl dosing (Dose-4). Figure 7 compares the TMP rises. PACl-B70S led to a 16-kPa rise of TMP during filtration, a rise that was much less than the 40-kPa rise when PACl-B50S was used. The implication is that the sulfated PACl with a higher basicity suppressed the rise of TMP much more effectively. This result is in accordance with a previous finding for ceramic filtration that high-basicity (71%) sulfated PACl performs better than normal basicity (51%) sulfated PACl in mitigating hydraulically irreversible fouling and suppressing a rise of TMP as well as in removing NOM because of its high charge neutralization capacity [27].

The non-sulfated PACls suppressed a rise of TMP in the order B20 $\approx$ B40 > B50 > B00 > B70, though the differences were small compared with that observed with the

sulfated PACls. Higher basicity did not help to suppress a rise of TMP. Figure 8 shows the concentrations of DOC, UV260, biopolymers, and humic substances. The removal rates of DOC, UV260, and humic substances were 30–40% between the raw water and filtrates for all the PACls. Differences of basicity between the in-house PACls did not result in any difference in the quality of these filtrates. The removal rates of biopolymers exceeded 90%, regardless of the basicity of the PACls, although biopolymer removal was slightly better with B20 than with the others. Because the differences of the TMPs were not large, the differences of water quality might have been difficult to see.

A comparison of sulfated and non-sulfated PACls revealed that the sulfated, high-basicity PACl (PACl-B70S) was superior to the non-sulfated, high-basicity PACl (PACl-B70), but the sulfated, normal-basicity PACl (PACl-B50S) was inferior to the non-sulfated, normal-basicity PACl (PACl-B50). The sulfated, high-basicity PACl (70%) and the none-sulfated, low-to-medium-basicity PACls (20% and 40%) showed the best performance. It has been reported that the non-sulfated, high-basicity PACl has a high charge-neutralization capacity but a low floc-formation ability because of its low rate of hydrolysis [28]. It is therefore not surprising that the non-sulfated, high-basicity PACl (PACl-B70) was less effective in suppressing TMP rise than the sulfated, high-basicity PACl (PACl-B70S). However, the hydrolysis rate increases with decreasing basicity [28]. Therefore, the non-sulfated, normal-basicity PACl suppressed TMP rise better than the non-sulfated, high-basicity PACl with decreasing basicity, although the charge neutralization capacity decreases with decreasing basicity [29]. The inferiority of the zero-basicity PACl (aluminum chloride solution) is probably due to its very low charge-neutralization capacity. The inferiority of the sulfated, normal-basicity PACl (PACl-B50S) compared to the non-sulfated, normal-basicity PACl (PACl-B50) could be explained by the fact that a sulfated PACl has a lower charge neutralization capacity than a non-sulfated PACl [30]. The higher the basicity of the sulfated PACl, the greater the charge-neutralization effect [31], and thus the greater the suppression of TMP rise. Even though the charge neutralization effect of the non-sulfated PACl increased with increasing basicity, its rate of hydrolysis would become relatively low [29,32]. Among non-sulfated PACls, therefore, those with medium basicity would probably be most effective in suppressing TMP rise, but the difference in effectiveness would probably be small. To further investigate the effectiveness of different PACls, we conducted a batch experiment

to reproduce conditions inside the submerged tank and measured floc particle sizes associated with different types of PACls. Figure 12S and Fig. 13S of the SI show the results. The sizes of the floc particles associated with the PACls were not very different. Flocs that form rapidly and consist of large particles are considered to have a better coagulation effect [28] that might be related to better suppression of TMP rise. However, the floc particle measurements and observations during application of PACls with different basicities were not consistent with the increases of the TMP in the filtration experiments. Further studies are needed not only on the size of floc particles but also on membrane foulants and their removability as a function of coagulant properties.

4. Conclusions

(1) Changing the precoat filtration flux after pulse dosing of SSPAC did not have a significant effect on suppression of TMP rise. However, a slow or constant flux rather than a high flux is recommended to suppress TMP rise because the precoat layer that is formed can be cleaned off by hydraulic backwashing more easily.

(2) Dosing with PACl throughout the raw water feed and the whole filtration process was the most effective of the various dosing schedules for suppressing TMP rise. While pulse dosing of SSPAC was effective in suppressing TMP rise, pulse dosing of PACl coagulant was not because it resulted in excessively large floc particles that settled to the bottom of the membrane tank, where they influenced the formation of the precoat layer.

(3) Feeding the submerged tank initially with treated water before filtration began was more effective in suppressing TMP rise than normally applying raw water by minimizing contact between NOM and the membrane surface during the precoating period.

(4) A sulfated PACl with high basicity (70%) seemed to be more effective in suppressing a rise of TMP than one with medium-basicity (50%). However, for non-sulfated PACls, low-to-medium-basicity PACls (20% and 40%) more effectively suppressed TMP rise than PACls with basicities of 0% and 70%.

Acknowledgments

This work was supported by supported by a JSPS Grant-in-Aid for Scientific Research S (no. 16H06362) and A (no. 21H04567) and by JST SPRING (no. JPMJSP2119). The authors gratefully acknowledge Futamura Chemical for providing PAC samples; Taki Chemical for coagulants; Ibaraki Prefectural Waterworks Bureau for water samplings.

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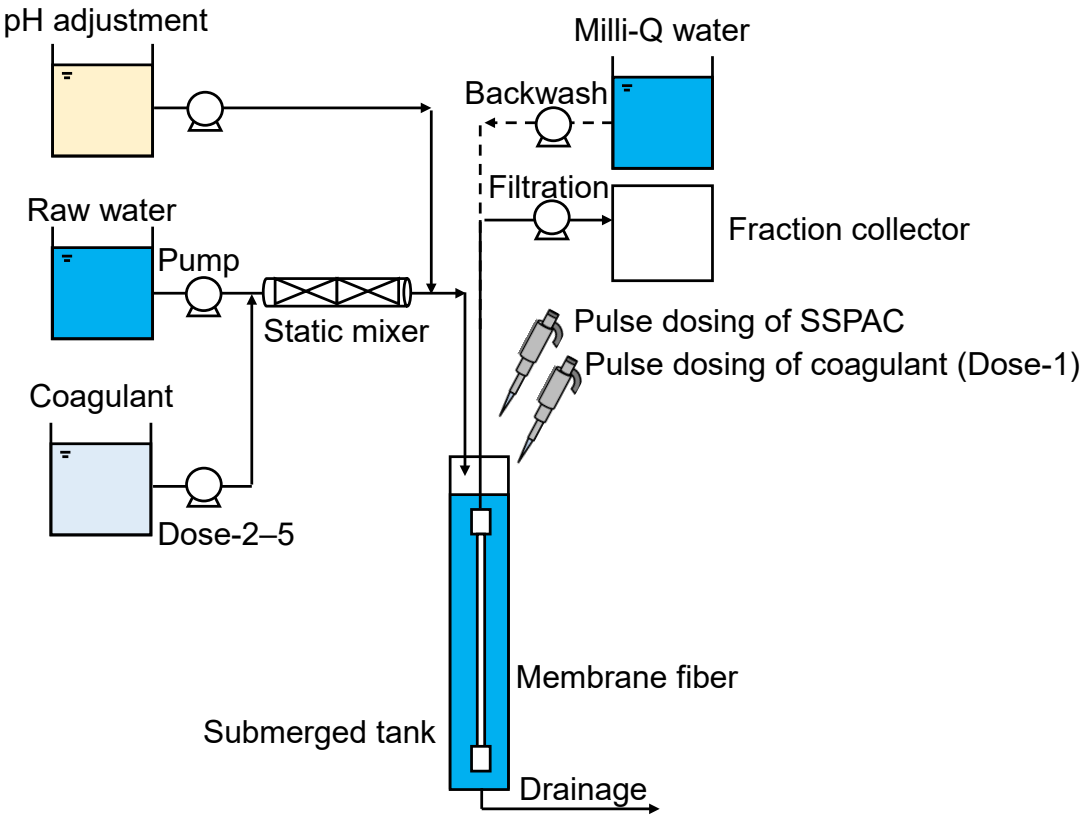

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544 Fig. 1. Experimental setup for submerged filtration.

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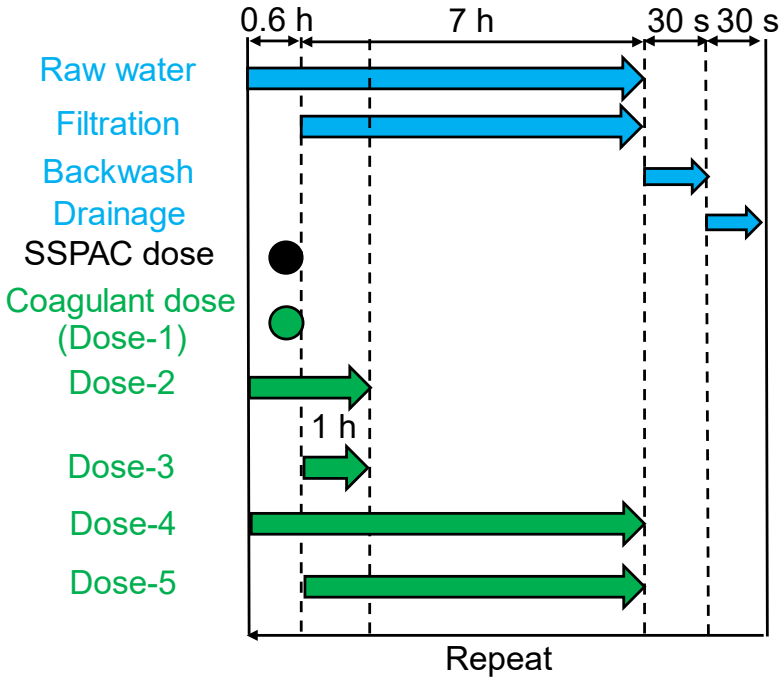

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550 Fig. 2. Dose timing of coagulant.
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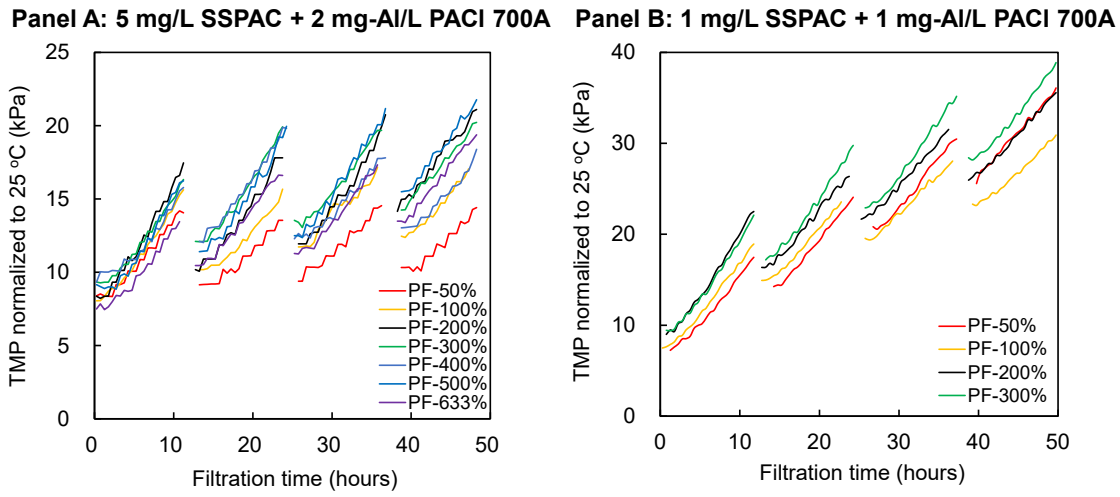

Fig. 3. Transmembrane pressure (TMP) versus filtration time. Submicron super-fine powdered activated carbon (SSPAC) was dosed every 12 hours in a pulse at the beginning of each cycle of filtration after the backwash. After the pulse dose of SSPAC, filtration was conducted at the precoat filtration flux, and then the filtration flux was returned to the main filtration flux of 1.7 m/day (70.8 L m^{-2} h^{-1}). For example, in the PF-50% run, the precoat filtration flux was 50% of the main filtration flux. PACl-B70S coagulant was dosed continuously (Dose-4 in Fig. 2, Section 2.4.3). SSPAC-1 and Water-2 were used in Panel A and SSPAC-2 and Water-3 were used in Panel B. The SSPAC and coagulant dosages were 5 mg/L and 2 mg-Al/L, respectively, in Panel A and 1 mg /L and 1 mg-Al/L, respectively, in Panel B. Panel A: experiments were conducted three times with PF-100% and twice with PF-300% and PF-633% for reproducibility. The average values were then calculated. Panel B: experiments were conducted two or three times for each condition, and the average values were then calculated (Fig. 5S in the SI shows all data).

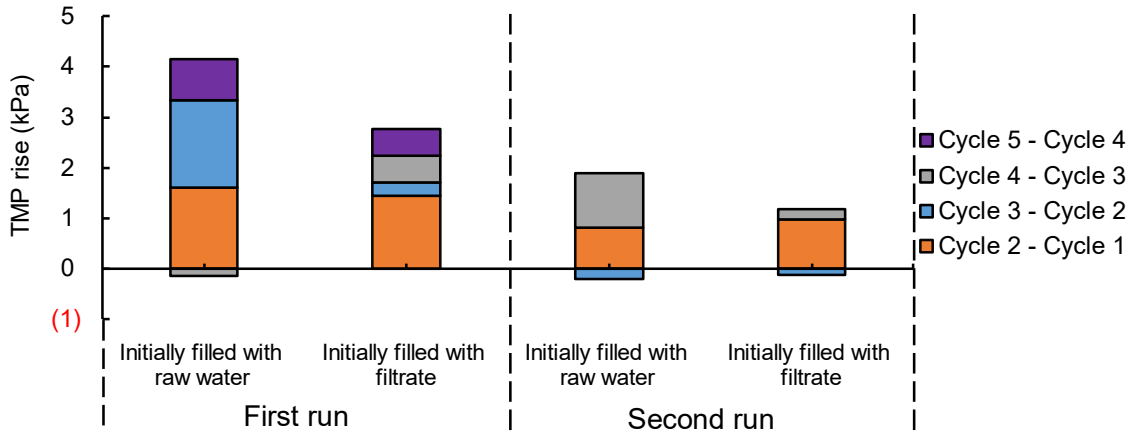

Fig. 4. Comparison of transmembrane pressure (TMP) rises due to hydraulically-irreversible membrane fouling, which was determined as the differences of the initial TMPs of two consecutive batches of filtration process with backwashing in between by two methods (submerged tank was fed with raw water or treated water before the filtration begin). The changes of TMP against time are shown in Fig. 8S, SI.

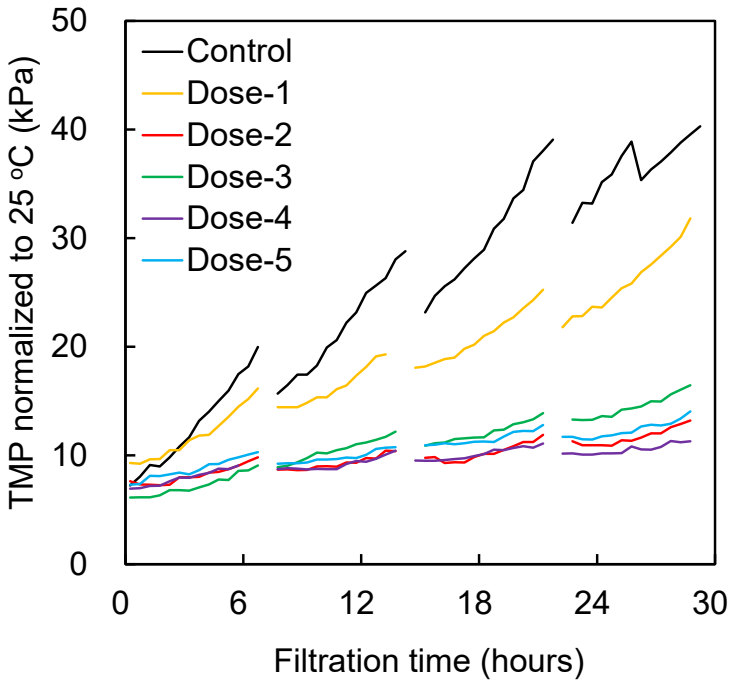

Fig. 5. Transmembrane pressure (TMP) versus filtration time. Submicron super-fine powdered activated carbon (SSPAC) was dosed every 7 hours in a pulse at the beginning of each cycle of filtration after the backwash. The Control data indicate the results of the control experiment without dosing of SSPAC or coagulant. The dose methods are explained in Section 2.4.3 and Fig. 2. The filtration rate was 1.7 m/day (70.8 L m^{-2} h^{-1}). The reagents were PACl-B70S, SSPAC-1, and Water-1. The SSPAC and coagulant dosages were 5 mg/L and 2 mg-Al/L, respectively.

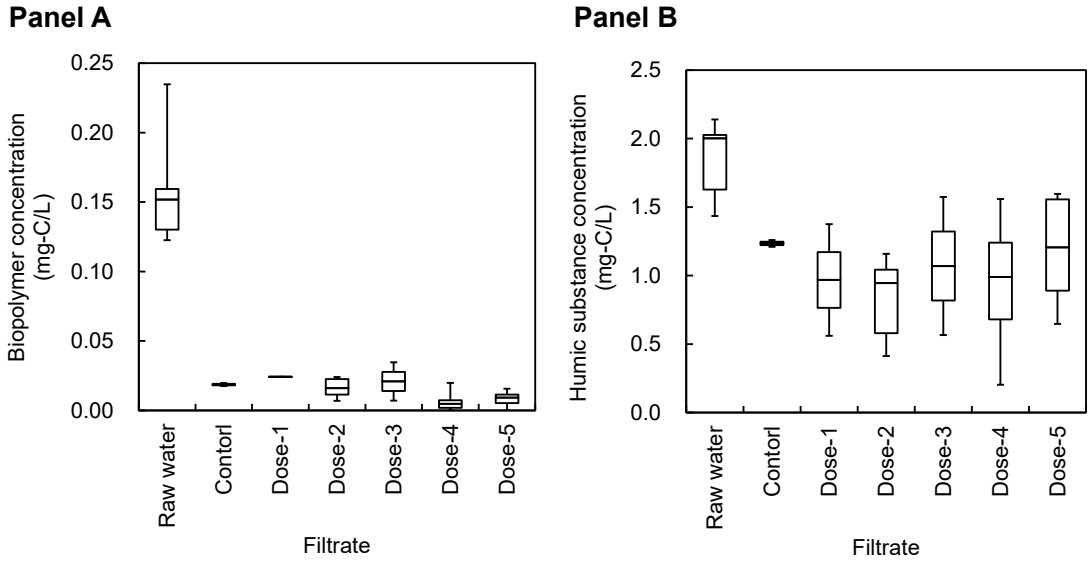

Fig. 6. Box-and-whisker plots of concentrations of biopolymer and humic substances in raw water and filtrates. Dosing of submicron super-fine powdered activated carbon (SSPAC) and coagulant were omitted in the Control experiment. SSPAC was dosed every 7 hours in a pulse at the beginning of each batch of filtration after the backwash. The reagents were PACl-B70S, SSPAC-1, and Water-1. The SSPAC and coagulant dosages were 5 mg/L and 2 mg-Al/L, respectively. The dose methods are explained in Section 2.4.3 and Fig. 2. Horizontal lines within boxes represent median values, the upper and lower horizontal lines in the boxes represent the 75th and 25th percentiles, respectively. The upper and lower bars outside the boxes indicate the maximum and minimum values, respectively.

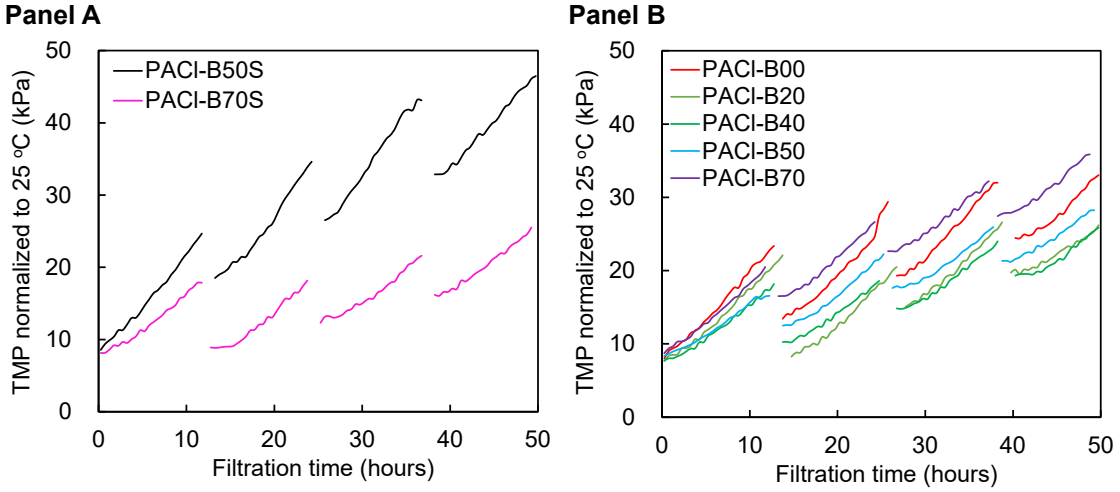

Fig. 7. Transmembrane pressure (TMP) versus filtration time. Submicron super-fine powdered activated carbon (SSPAC) was dosed every 12 hours in a pulse at the beginning of each batch of filtration after the backwash. The experiments were conducted by using various coagulants (Section 2.3) by the Dose-4 method described in Section 2.4.3. In Panel A, commercially available polyaluminum chlorides (PACl) with basicity of 50% (PACl-B50S) and 70% (PACl-B70S) with sulfate ions were used. In Panel B, in-house PACl with basicity of 0% (PACl-B00), 20% (PACl-B20), 40% (PACl-B40), 50% (PACl-B50) and 70% (PACl-B70) without sulfate ions were used. Filtration rate was 1.7 m/day (70.8 L m^{-2} h^{-1}). SSPAC-2 and Water-3 were used. SSPAC and coagulant dosages were 1 mg /L and 1 mg-Al/L, respectively.

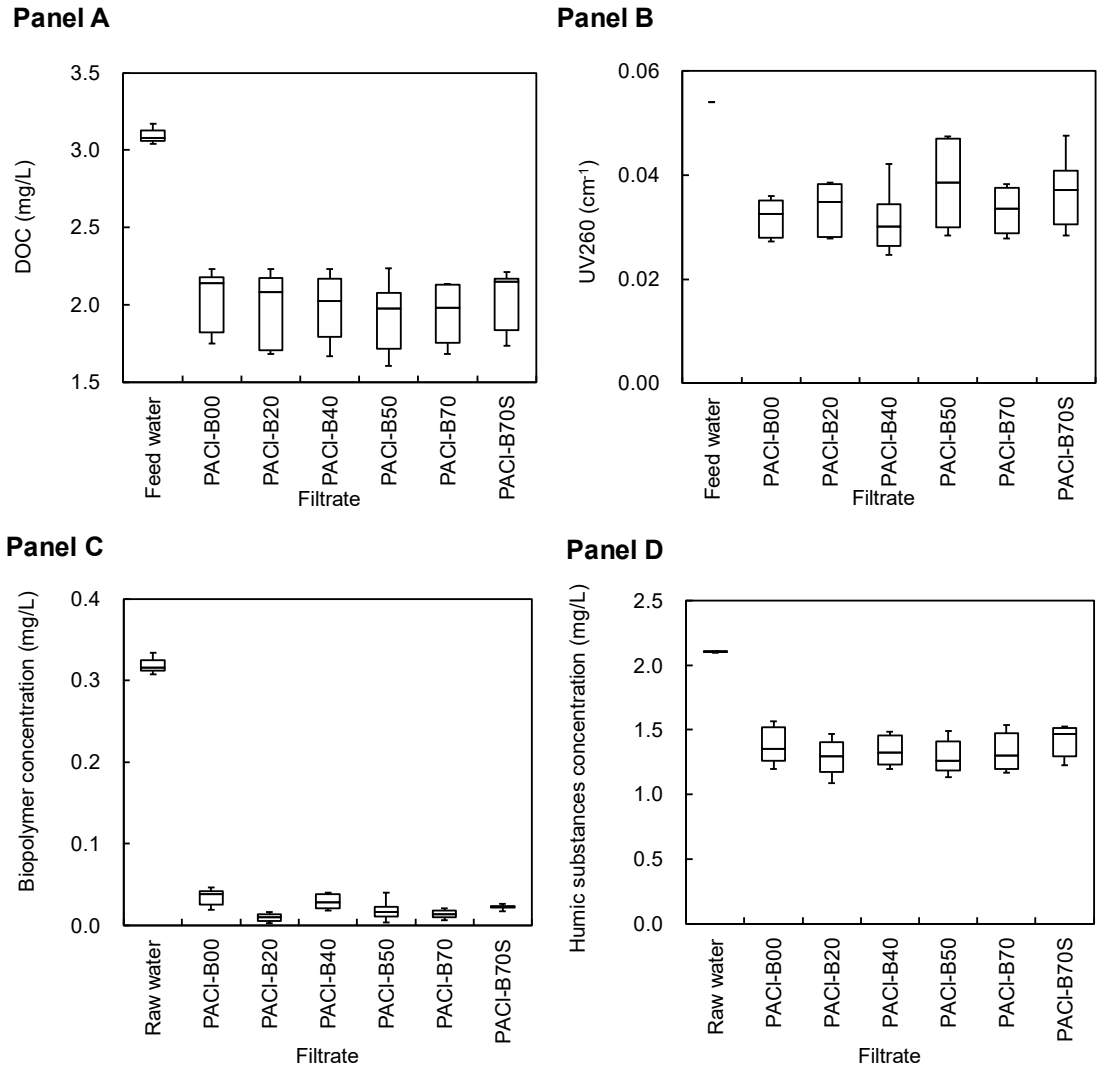

Fig. 8. Box-and-whisker plots of concentrations of dissolved organic carbon (DOC) (Panel A), UV260 (Panel B), biopolymers (Panel C) and humic substances (Panel D) in feedwater and filtrates. Sulfated polyaluminum chlorides (PACls) with a basicity of 70% (PACl-B70S) and non-sulfated PACls with different basicities were used (PACl-B00, B20, B40, B50, and B70). There are no data for PACl-50S because samples were unavailable. Submicron super-fine powdered activated carbon (SSPAC) was dosed using the Dose-4 method (Section 2.4.3 and Fig. 2) every 12 hours in a pulse at the beginning of each batch of filtration after the backwash. The reagents were SSPAC-2 and Water-3. The SSPAC and coagulant dosages were 1 mg /L and 1 mg-Al/L, respectively. Horizontal lines within boxes indicate median values, and the upper and lower horizontal lines in the boxes indicate the 75th and 25th percentiles, respectively. The upper and lower bars outside the boxes indicate the maximum and minimum values, respectively.

Supplementary Information

Suppressing transmembrane-pressure rise by pulse dosing of submicron super-fine powdered activated carbon: effects of filtration flux, coagulant types, and coagulant-dose timing during precoating

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Table 1S

Water quality.

	pH	DOC mg/L	UV abs. at 260 nm cm^{-1}	Biopolymer mg/L	Alkalinity mg/L as $CaCO_3$	Na^+ mg/L
Water-1	7.62	2.66	0.060	0.0800	72.0	43.7
Water-2	7.91	3.45	0.070	0.340	68.0	41.6
Water-3	7.17	3.08	0.054	0.280	68.0	38.7
Water-4	7.96	3.69	0.070	0.360	71.0	43.8

	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L
Water-1	5.84	9.18	18.0	54.0	13.8	22.3
Water-2	5.48	8.61	17.3	41.3	14.1	28.0
Water-3	4.83	8.39	16.0	41.2	n/a	19.8
Water-4	5.55	9.25	17.9	51.6	n/a	14.8

Measurements other than pH were taken after membrane filtration (Water-1: 0.1-µm MCE (mixed cellulose ester) membrane. Water-2, Water-3 and Water-4: 0.45-µm PTFE (polytetrafluoroethylene) membrane).

Table 2S

Conditions during coagulant production. (Sodium carbonate was not added during the production of PACl-B00, B20, and B40 for basicity adjustment.)

Name of coagulants	Adjustment of basicity						
	Temperature °C	Time min	2M sodium carbonate mL	Al mol/L	Cl/Al	Na/Al	Basicity %
PACl-B00				1.85	3.30		0
PACl-B20				2.35	2.29		20
PACl-B40				3.15	1.74		40
PACl-B50	75	50	1.47	3.62	1.68	0.183	50
PACl-B70	75	44	6.25	2.35	1.66	0.759	70

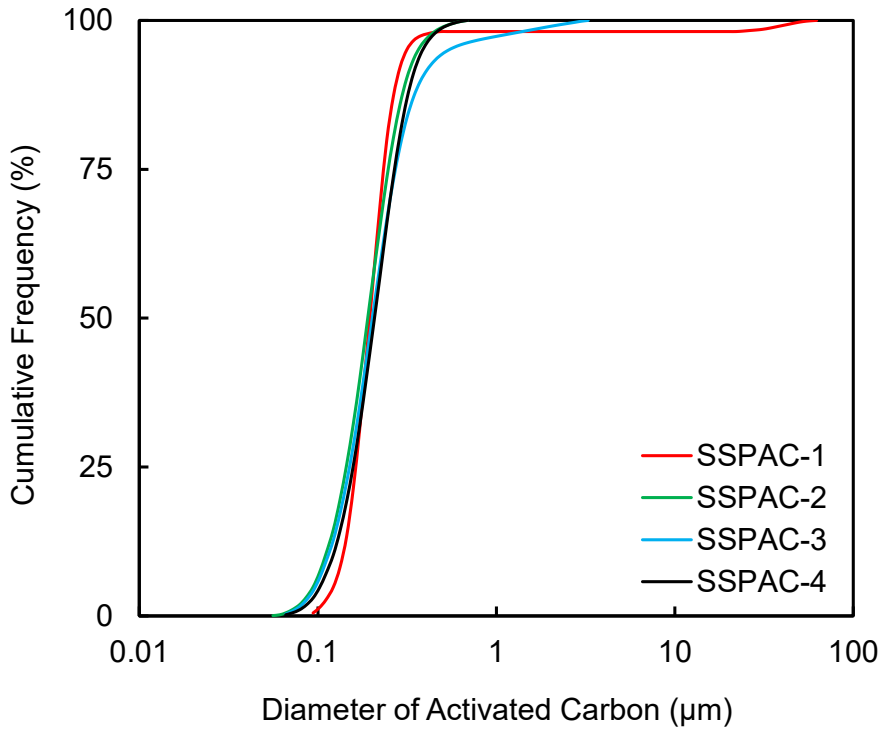

Fig. 1S. Particle size distributions of submicron super-fine powdered activated carbon (SSPAC). Use of SSPAC-1 and SSPAC-4 are discussed in Section 3.1, use of SSPAC-2 in Section 3.2, and use of SSPAC-3 in Section 3.3.

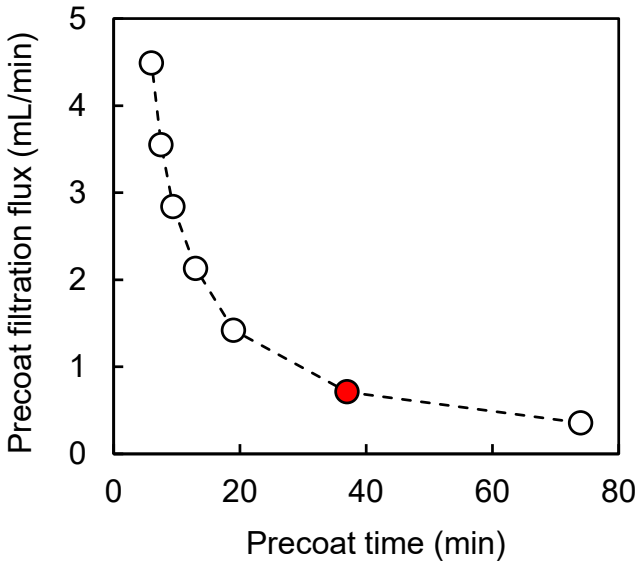

Fig. 2S. Change of precoat filtration flux against precoat time. The red dot indicates the main filtration flux (1.7 m/day corresponds to 0.71 mL/min in this figure).

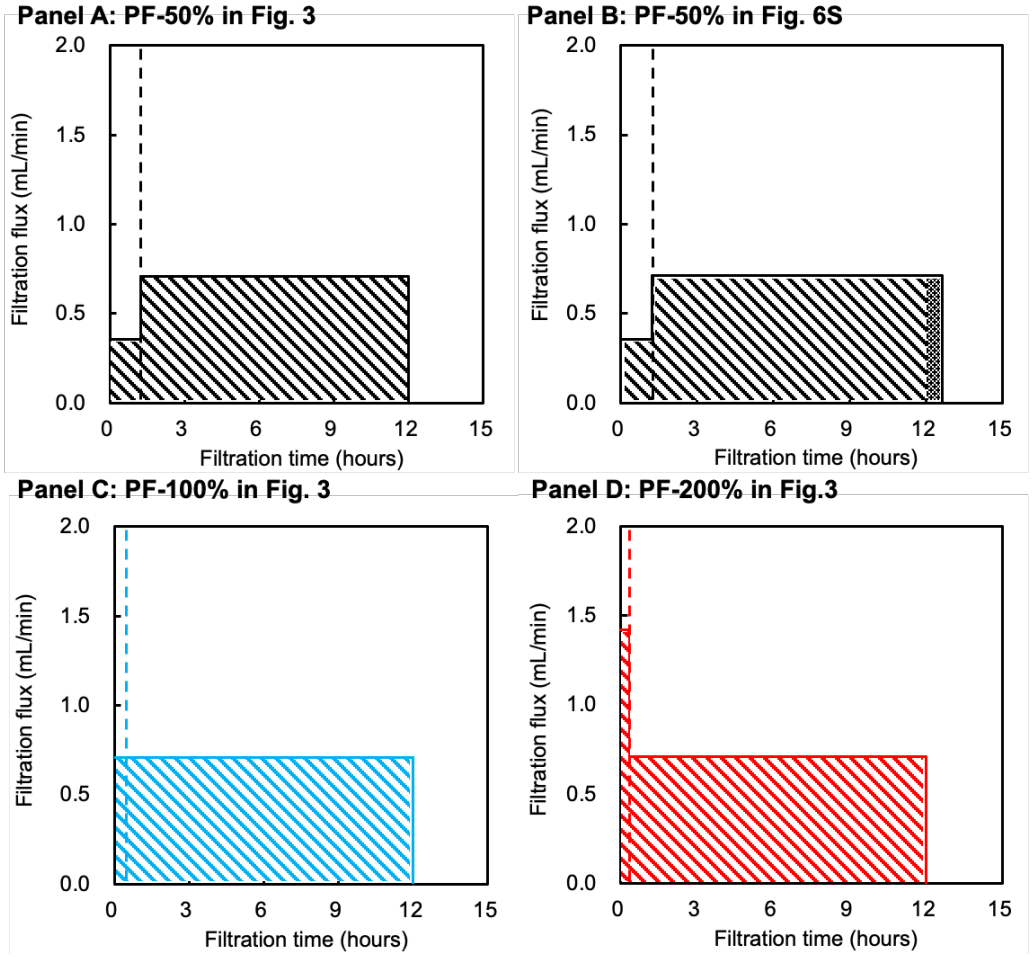

Fig. 3S. Change of filtration flux against filtration time. Panels A, C, and D correspond to the experimental conditions of Fig. 3. Panel B corresponds to Fig. 6S of the SI, where the filtration time has been slightly extended (dotted part) because the amount of filtered water was adjusted to be the same as in the case of PF-100%. PF indicates precoat filtration, and the percentage indicates the ratio of precoat filtration flux to main filtration flux. The dashed line indicates the end of the precoat period and the start of main filtration.

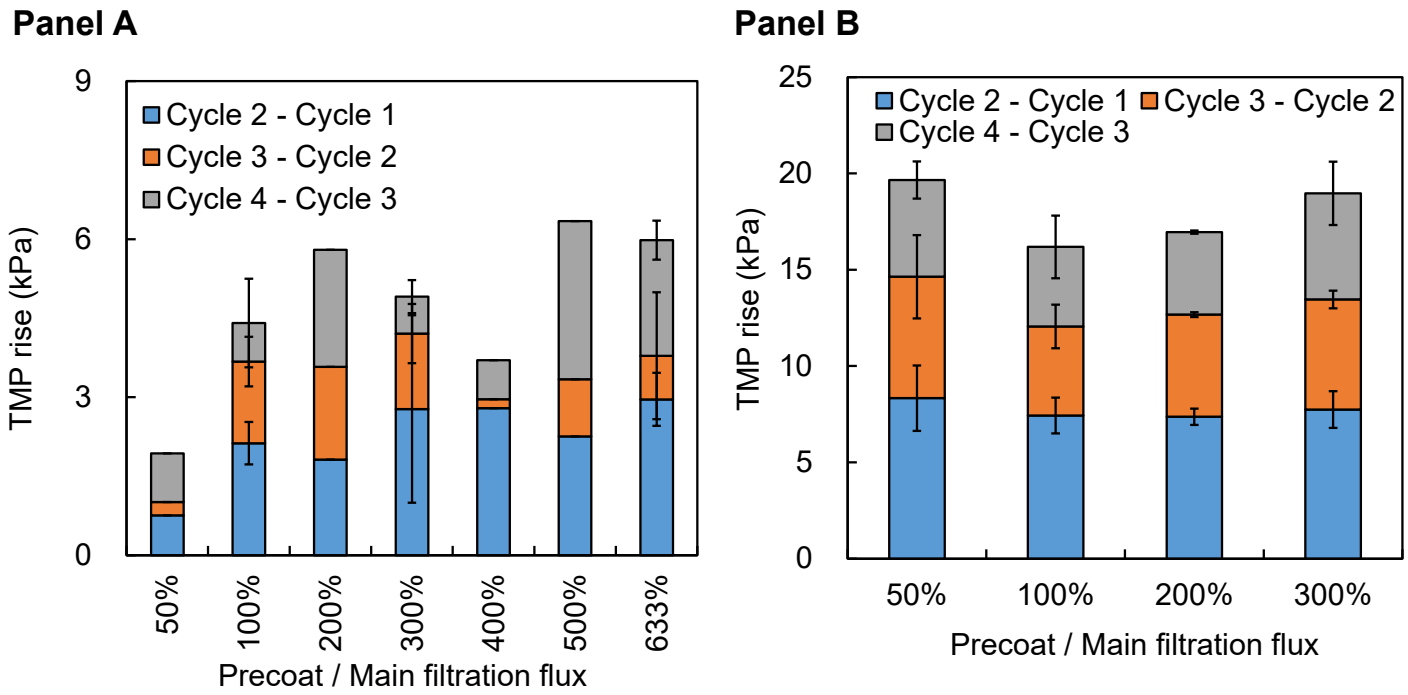

Fig. 4S. Transmembrane pressure (TMP) rise due to hydraulically irreversible membrane fouling, which was determined as the differences of the initial TMPs of two consecutive batches of the filtration process with backwashing in between. Panel A and Panel B in this figure correspond to Panel A and Panel B of Fig. 3, respectively. Error bars indicate standard deviations.

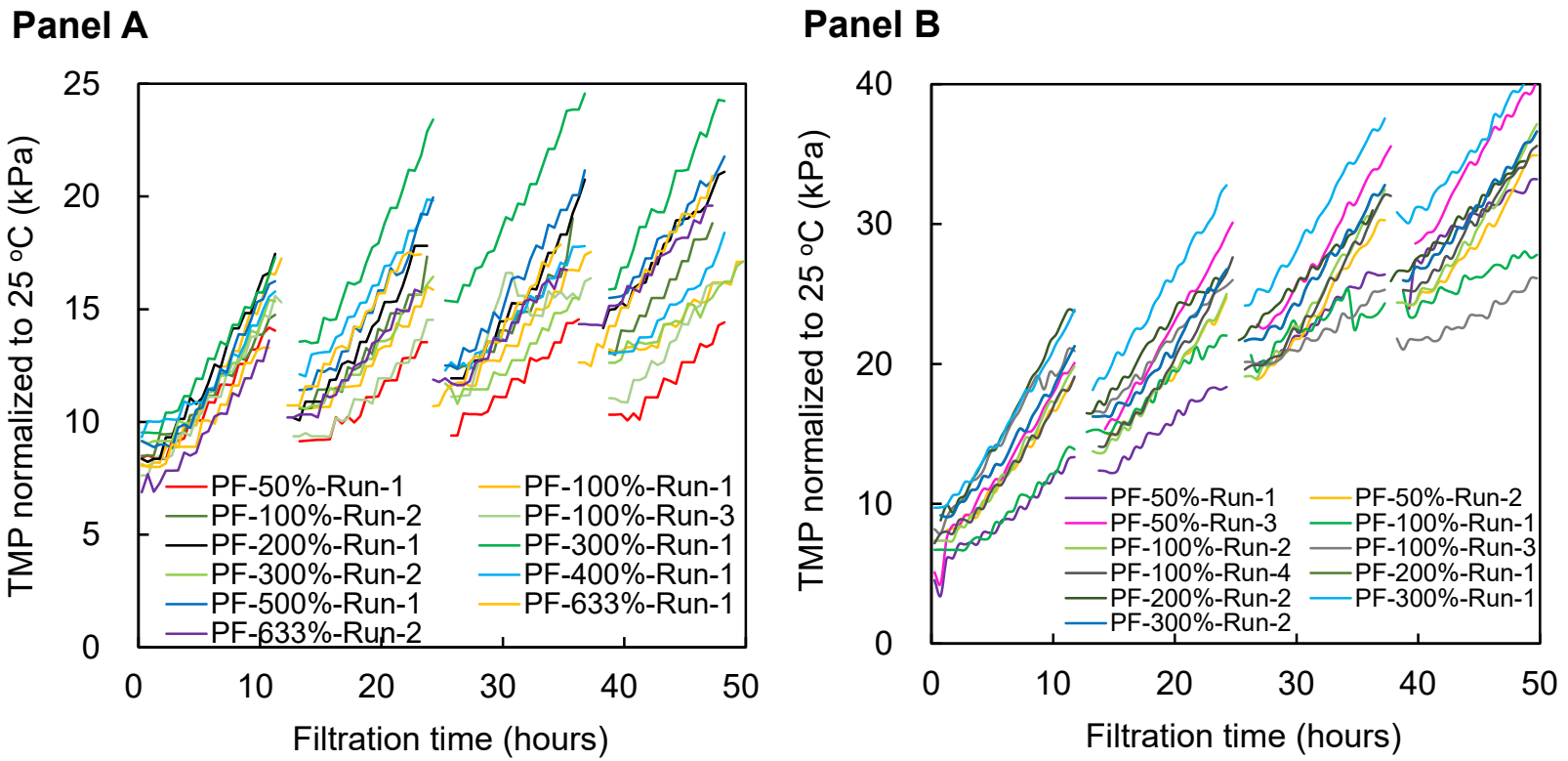

Fig. 5S. Transmembrane pressure (TMP) versus filtration time. Submicron super-fine powdered activated carbon (SSPAC) was dosed in a pulse at the beginning of each batch of filtration after a backwash every 12 hours. After the pulse dosing of SSPAC, filtration was conducted at the precoat filtration flux, and then the filtration flux was returned to the main filtration flux of 1.7 m/day (70.8 L m^{-2} h^{-1}): for example, in the PF-50% run, the precoat filtration flux was 50% of the main filtration flux. The PACl-B70S coagulant was dosed continuously (Dose-4 in Fig. 2, Section 2.4.3). SSPAC-1 and Water-2 were used in Panel A, and SSPAC-2 and Water-3 were used in Panel B. SSPAC and coagulant dosages were 5 mg/L and 2 mg-Al/L in Panel A and 1 mg /L and 1 mg-Al/L in Panel B, respectively.

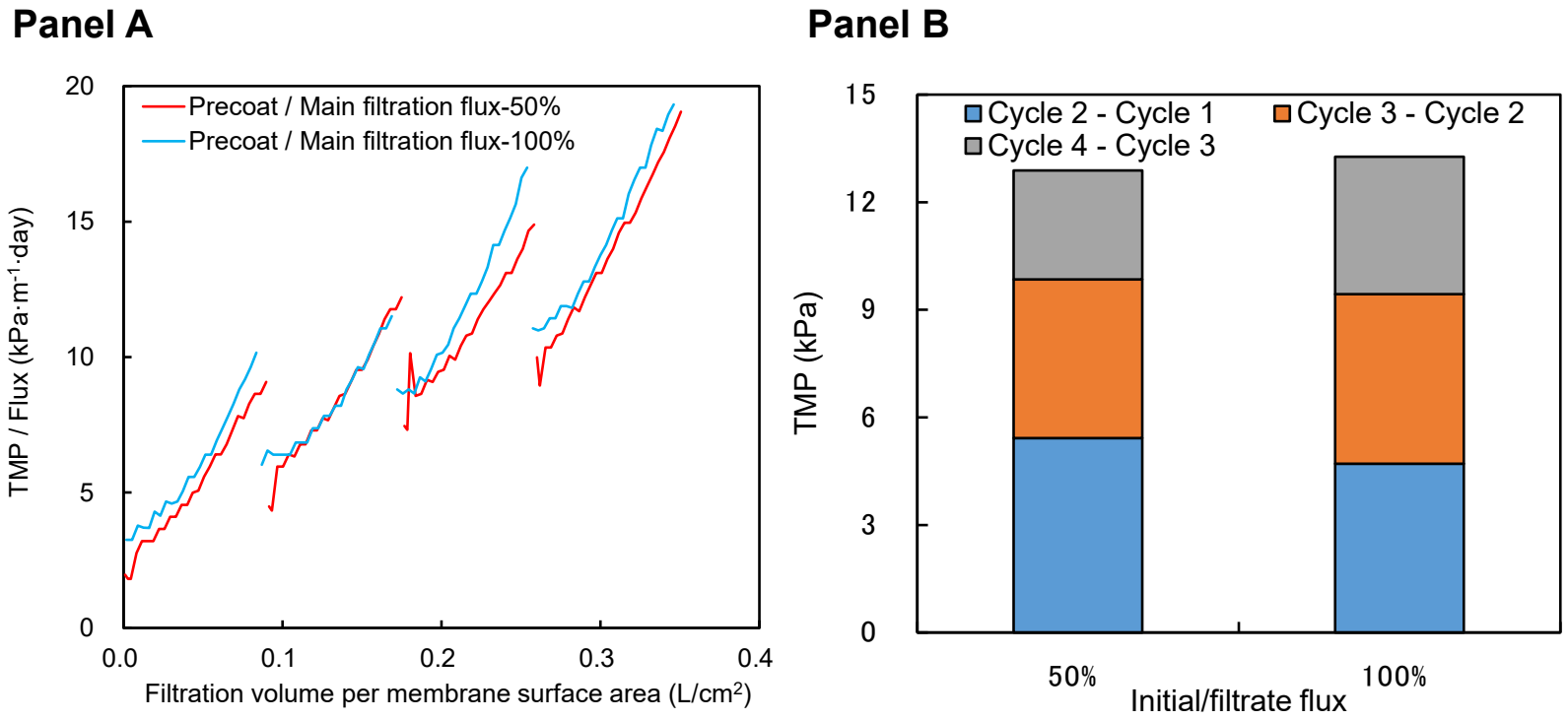

Fig. 6S. Normalized transmembrane pressure (TMP/flux) versus filtration volume per membrane surface area (Panel A). TMP rise due to hydraulically irreversible membrane fouling, which was determined as the differences between the initial TMPs of two consecutive batches of filtration process with backwashing in between (Panel B). Submicron super-fine powdered activated carbon (SSPAC) was dosed at the beginning of each batch of filtration after a backwash every 12 hours. The experiments were conducted by using PACl-B70S with Dose-4 in Section 2.4.3. Filtration rate was 1.7 m/day (70.8 L m^{-2} h^{-1}). SSPAC-4 and Water-4 were used. Coagulant and SSPAC dosages were 2 mg-Al/L and 5 mg/L. In Panel B, no significant difference in TMP was found between PF-50% and 100% ($p > 0.05$ based on a Student's *t*-test).

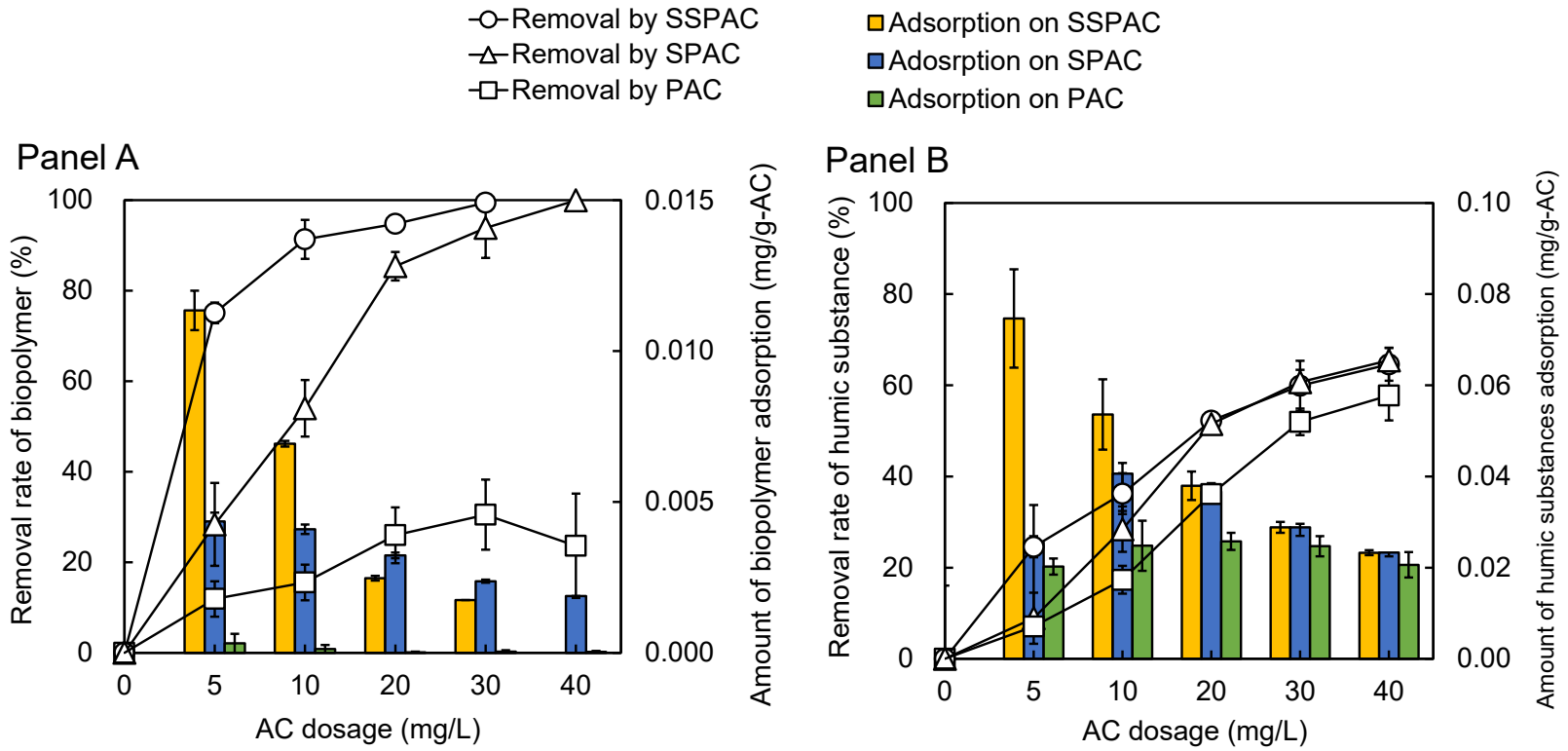

Fig. 7S. Removal rate and adsorption amount of biopolymer (Panel A) and humic substance (Panel B) as a function of AC dosage. Adsorption isotherm experiment was conducted at room temperature (20°C) for one week.

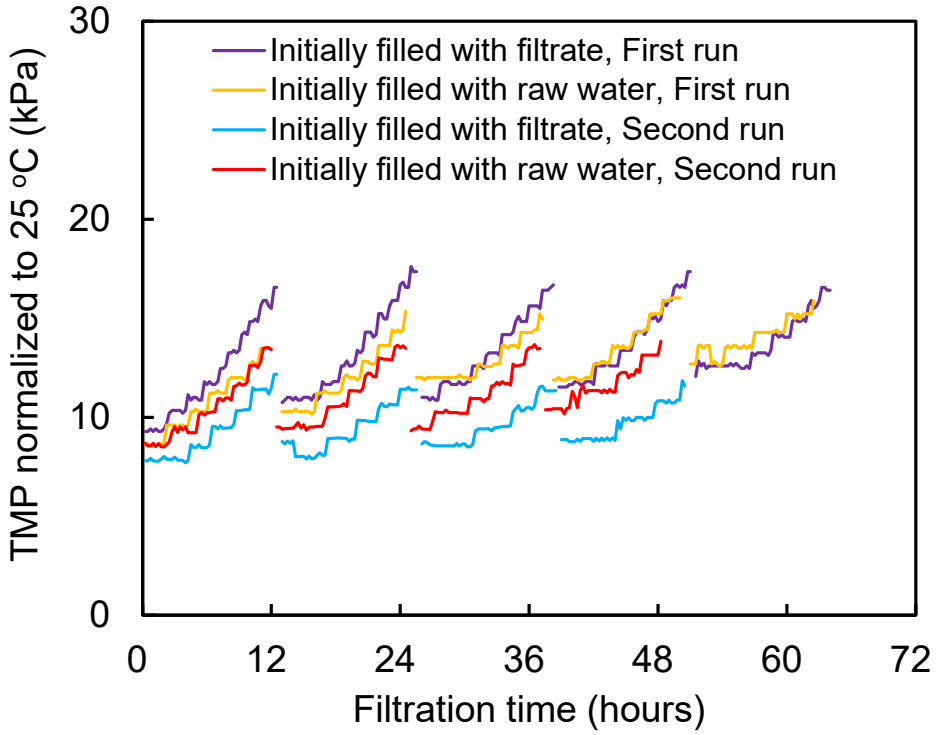

Fig. 8S. Transmembrane pressure (TMP) rise versus filtration time. Before filtration began, the submerged tank was filled with either coagulation-pretreated raw water or filtrate. SSPAC (submicron super-fine powdered activated carbon) was dosed in a pulse at the beginning of each batch of filtration after the backwash of every 12 hours. Filtration rate was 1.7 m/day (70.8 L m^{-2} h^{-1}). PACl-B70S, SSPAC-4, Water-4 were used. SSPAC and coagulant dosages were 5 mg/L and 2 mg-Al/L.

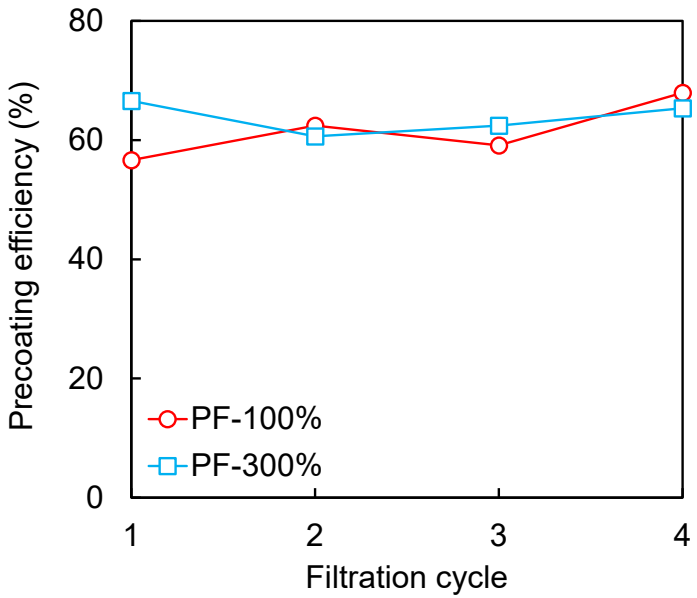

Fig. 9S. Precoating efficiency: SSPAC (submicron super-fine powdered activated carbon) attached to membrane expressed as percentage of dosed SSPAC. The experiments were conducted by using PACl-B70S with Dose-4 in Section 2.4.3. Filtration rate was 1.7 m/day (70.8 L m^{-2} h^{-1}). SSPAC-2 and Water-3 were used. Coagulant and SSPAC dosages were 1 mg-Al/L and 1 mg/L.

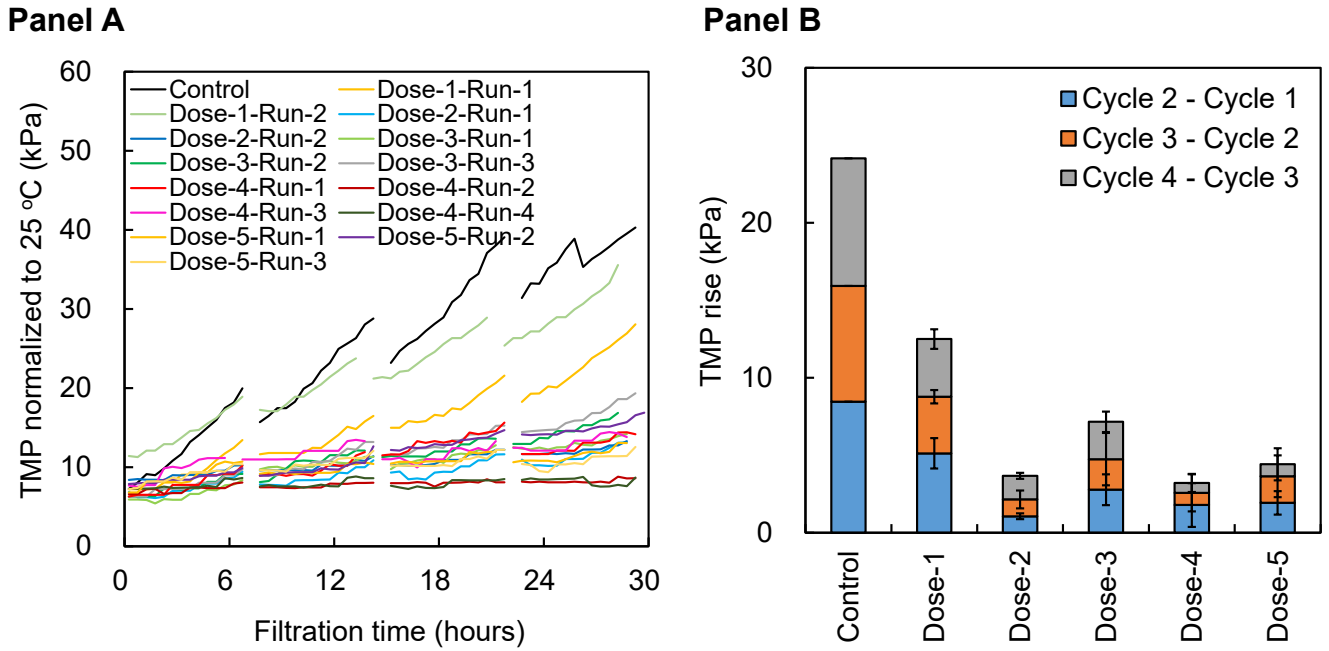

Fig. 10S. Transmembrane pressure (TMP) versus filtration time (Panel A). TMP rise due to hydraulically irreversible membrane fouling, which was determined as the differences between the initial TMPs of two consecutive batches of the filtration process with backwashing in between (Panel B). Submicron super-fine powdered activated carbon (SSPAC) was dosed in a pulse at the beginning of each batch of filtration after a backwash every 7 hours. Dose-1 indicates pulse dosing of coagulant right after pulse dosing of SSPAC. Dose-2 indicates continuous dosing of coagulant during both the water feeding of submerged tank and 1 h from the start of filtration. Dose-3 indicates continuous dosing of coagulant only during 1 h from the start of filtration. Dose-4 indicates continuous dosing of coagulant during both the water feeding of submerged tank and the whole filtration period. Dose-5 indicates continuous dosing of coagulant during filtration period only. The dose methods are explained in Section 2.4.3 and Fig. 2. Filtration rate was 1.7 m/day (70.8 L m^{-2} h^{-1}). PACl-B70S, SSPAC-1, and Water-1 were used. SSPAC and coagulant dosages were 5 mg/L and 2 mg-Al/L, respectively. Error bars indicate standard deviations among different runs.

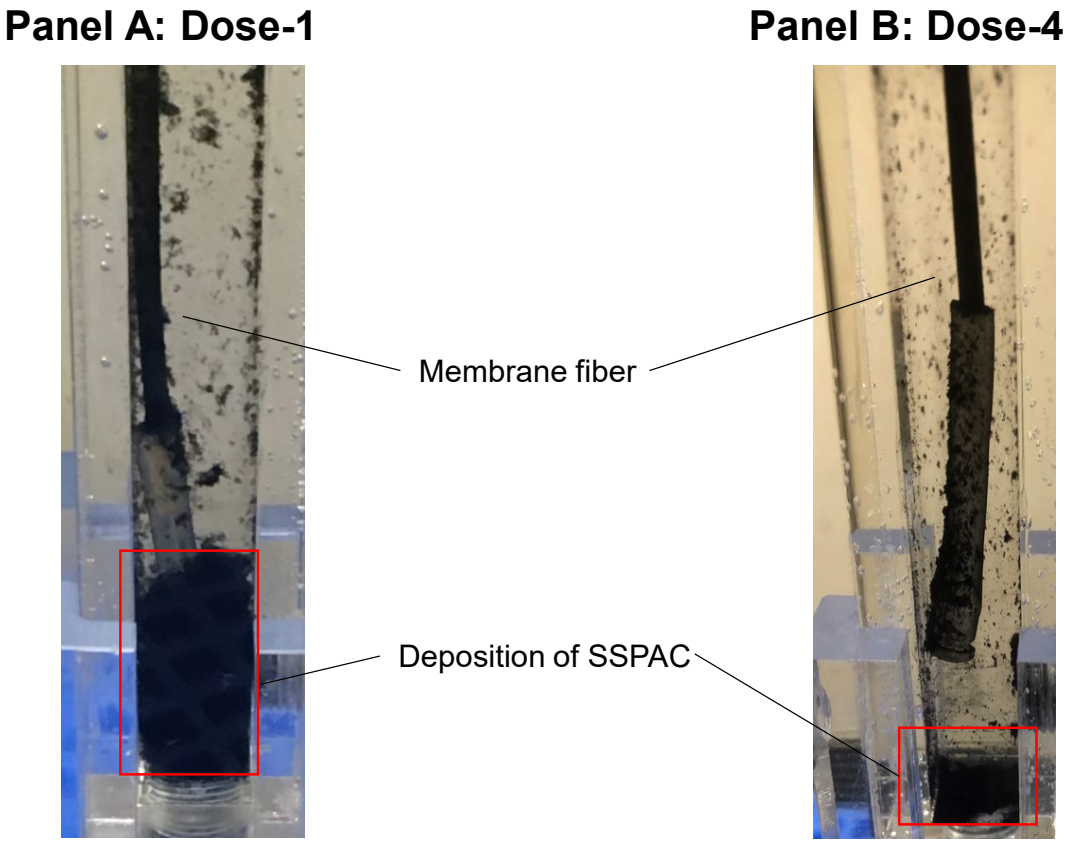

Fig. 11S. Photographs of the submerged tank during filtration after the precoat period. The experiments were conducted by using PACl-B70S with Dose-1 for Panel A and Dose-4 for Panel B, as explained in Section 2.4.3 and Fig. 2. The filtration rate was 1.7 m/day (70.8 L m^{-2} h^{-1}). SSPAC-1 and Water-1 were used. Coagulant and SSPAC dosages were 2 mg-Al/L and 5 mg/L, respectively.

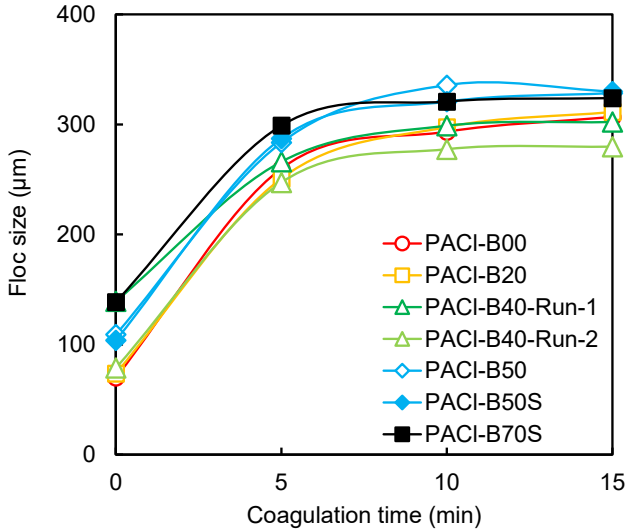

Fig. 12S. Floc size versus coagulation time. Submicron super-fine powdered activated carbon (SSPAC) was pulse dosed into a beaker with the raw water and coagulants to reproduce the conditions inside the submerged tank in Section 2.4.1. After 1 min of rapid mixing, floc particle size was measured every 5 min. The samples were circulated during the experiment. Sulfated polyaluminum chlorides (PACls) with basicity of 50% and 70% (PACl-B50S and 70S) and non-sulfated PACls with different basicities were used (PACl-B00, B20, B40, B50). There are no data for PACl-B70 due to unavailability of samples. SSPAC-2 and Water-3 were used. SSPAC and coagulant dosages were 1 mg /L and 1 mg-Al/L, respectively.

Floc particle-size measurements were conducted using a 1-L beaker (640 mL raw water) connected to a particle-size analyzer (Microtrac MT3300EXII, Nikkiso Co., Inc., Tokyo, Japan). Measurements were taken in triplicate over a 20-second period, and the average value was recorded. Unlike typical measurements with a Microtrac particle-size analyzer, ultrasonication was turned off to avoid breakage of the floc particles. The beaker and particle-size analyzer were connected by a tube with a 7.9-mm inner diameter. A peristaltic pump circulated water to avoid floc breakage. A photograph of floc particles was taken with a digital, single-lens reflex camera (EOS 60D; Canon Ltd., Tokyo, Japan).

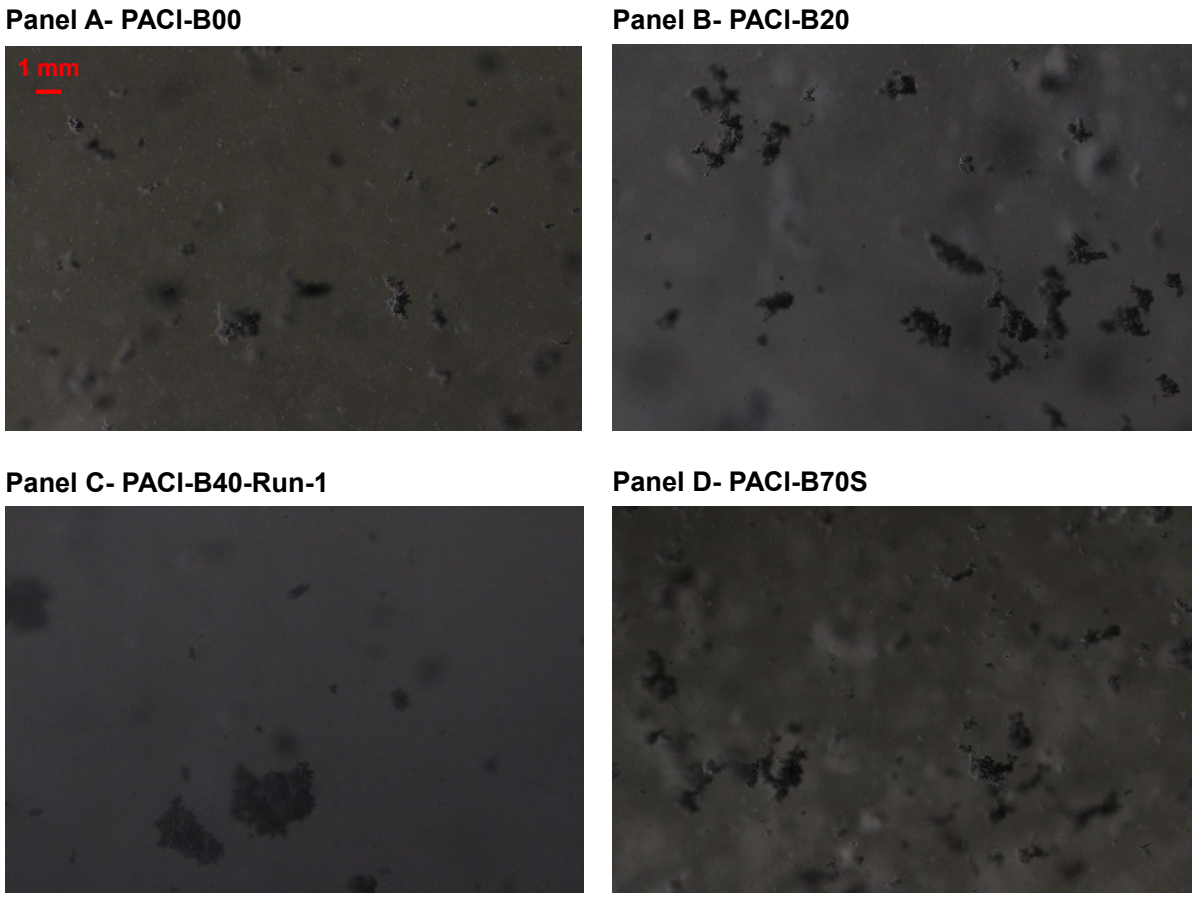

Fig. 13S. Photographs of the floc particles after the 15-min coagulation described in Fig. 12S, SI. Sulfated polyaluminum chlorides (PACls) with a basicity of 70% (PACl-B70S) and non-sulfated PACls with different basicities were used (PACl-B00, B20, and B40). No data for PACl-B50 and B70 due to unavailability of samples. The reagents were SSPAC-2 and Water-3. SSPAC and coagulant dosages were 1 mg /L and 1 mg-Al/L, respectively.